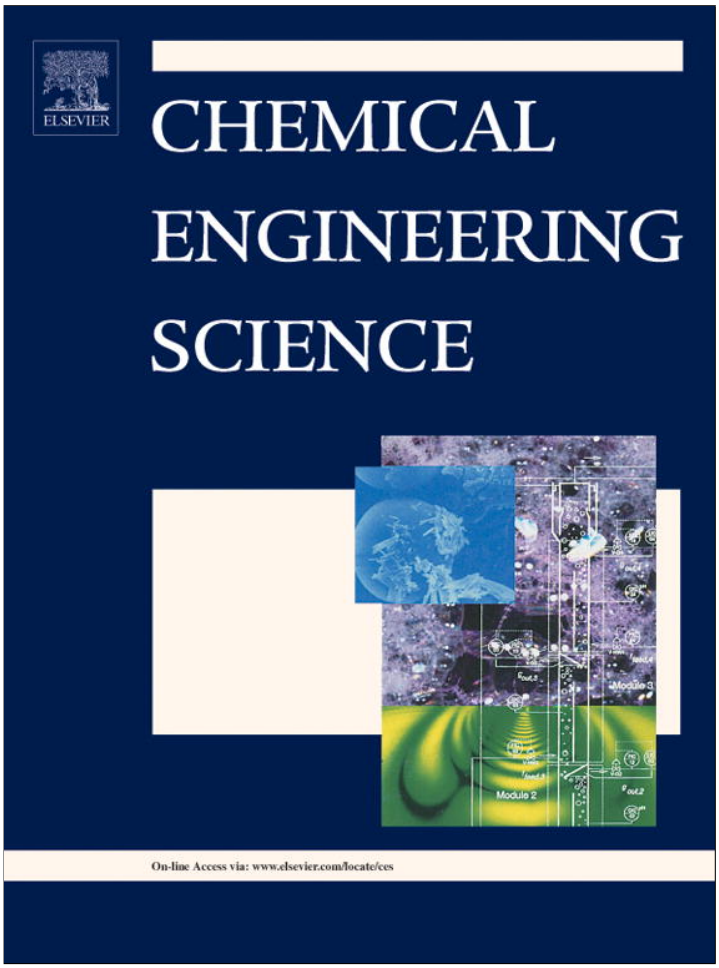

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A novel phosphonium-based deep eutectic catalyst for biodiesel production from industrial low grade crude palm oil

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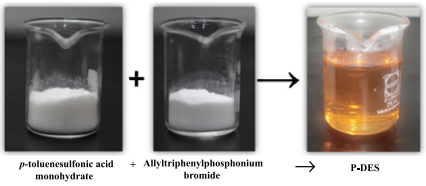
HIGHLIGHTS

- Deep eutectic solvent (DES) is introduced as a novel catalyst for biodiesel production.
- Allyltriphenylphosphonium bromide is used for the first time in the preparation of DES.
- Phosphonium based-deep eutectic solvent (P-DES) can be recycled for esterification reaction four times.
- Biodiesel produced from low grade crude palm oil meets EN 14214 and ASTM D6751.
- P-DES can be used for many chemical reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

This study explores the possibility of producing low grade crude palm oil (LGCPO)-based biodiesel using a two-stage process in which a phosphonium-based deep eutectic solvent (P-DES) and an alkali are used as catalysts. The pre-treatment of LGCPO was conducted using a P-DES composed of a hydrogen bond donor (i.e. *p*-toluenesulfonic acid monohydrate) and a salt (i.e. allyltriphenylphosphonium bromide) as a novel recyclable catalyst. The P-DES was used in different dosages in the presence of methanol to reduce the level of free fatty acids (FFA) to the acceptable limit for alkaline transesterification reaction. Batch pre-treatment of LGCPO was carried out to study the influence of P-DES dosage (from 0.25 to 3.5% wt/wt). The effects of other operating parameters such as molar ratio, reaction temperature and reaction time on FFA content reduction, yield of treated LGCPO and FFA to FAME conversion were studied. The P-DES showed high catalytic activity in the pre-treatment of LGCPO. The lab scale investigation proved the viability of esterification and transesterification of oil using P-DES and alkaline catalysts. The biodiesel produced from LGCPO meets the international standards (ASTM D6751 and EN 14214). Three to four times recycling runs of P-DES were achieved without losing its activity. This study introduces a new generation of catalysts for possible batch esterification reaction using P-DES followed by an alkaline transesterification reaction. This study will open a new field for utilizing this strong acid-based DES catalyst for many chemical reactions and industrial applications.

1. Introduction

Biodiesel is a renewable biofuel made from oils or fats and can be used directly in the diesel engine (Ma and Hanna, 1999;

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Canakci, 2007). Biodiesel fuel is biodegradable, non-toxic and can reduce air pollutant emissions (Wang et al., 2000; Canakci and Gerpen, 2001; Kalam and Masjuki, 2002; Oh et al., 2012). Biodiesel is more expensive compared to petroleum diesel fuel (Canakci and Gerpen, 2001). Therefore, decreasing the total cost of biodiesel production is a focus point of research in this field. The raw material used is the main cost contributing factor in the biodiesel production process (Ma and Hanna, 1999). As a result, many studies used waste cooking oils and industrial oils such as sludge palm oil (SPO) and acidic crude palm oil (ACPO) for biodiesel production (Leung and Guo, 2006; Hayyan et al., 2010a, 2011a, 2011b, 2012a). Low grade crude palm oil (LGCPO) is an agro-industrial raw material generated from oil palm mills and was only considered for biodiesel production by very few studies. LGCPO is produced in huge amounts industrially by mills and it contains high free fatty acid (FFA), un-favored impurities and high moisture content. Therefore, pre-treatment of LGCPO *via* esterification is necessary for conversion of high FFA to fatty acid methyl ester (FAME).

Many types of catalysts were used to produce biodiesel including homogenous catalysts, e.g. sulfuric acid, as well as heterogeneous catalysts, e.g. ferric sulfate (Santos et al., 2010; Wang et al., 2007). Esterification and transesterification using the lipase enzyme as a biocatalyst was also used in the biodiesel production (Xun et al., 2007). Recently, ionic liquids (ILs) were used as catalysts and solvents in organic reactions such as esterification reaction (Yue et al., 2011). ILs were studied as catalysts to treat the crude palm oil for biodiesel production (Elsheikh et al., 2011; Man et al., 2013). However, the problem associated in using ILs in the biodiesel production is the high synthesis cost and complicated preparation procedures.

In recent years, deep eutectic solvents (DESs) were considered as a new generation of ILs, or their alternatives, which gained considerable interest in academic research and industrial applications. DES is cheaper than conventional ILs due to its simple preparation procedure (Cooper et al., 2004; Hayyan et al., 2012b). In addition, DES shared other environmental merits with ILs such as biodegradability and non-flammability (Hu et al., 2004; Abbott et al., 2008; Olivier-Bourbigou et al., 2010). DES can be prepared *via* mixing of hydrogen bond donor (HBD) (which can be a member of alcohols, carboxylic acids, amines or metal halides) such as urea and salt such as choline chloride (ChCl) (Abbott et al., 2003).

Recently, DESs were introduced to a variety of applications such as synthesis of zeolite (Cooper et al., 2004), adsorption complexes of copper and copper oxide (Rimsza and Corrales, 2012), drug solubilization vehicles (Morrison et al., 2009) and glycerol removal from biodiesel (Hayyan et al., 2010b). Limited studies were found in the literature for using DES as a catalyst in chemical reactions. For instance, ChCl based DES was used as a catalyst in the carbon–carbon bond formation in the rapid synthesis of β-hydroxy functionalized derivatives (Singh et al., 2012). $ChCl \cdot xZnCl_2$ was introduced as a catalyst in the transesterification reaction (Long et al., 2010). Phosphonium-based DES was used for removal of glycerol, removal of KOH catalyst from biodiesel and for liquid–liquid extraction (Shahbaz et al., 2011a, 2011b; Kareem et al., 2012). Nevertheless, there is no reported study for the use of DES as a recyclable catalyst for esterification of acidic oils with high FFA for biodiesel production. Consequently, the utilization of DES as potential catalysts is worth to be investigated for the esterification of low grade oils for biodiesel production. In this research, we demonstrate for the first time the utilization of phosphonium-based DES (P-DES) in the pre-treatment of low grade oils. The main goals of this study are (a) to study the potential use of LGCPO as by-product of industrial oil palm mills for biodiesel production; (b) to investigate the influence of P-DES dosage as a new recyclable catalyst; (c) to study the influence of molar ratio, reaction time and reaction temperature and (d) to evaluate the activity of P-DES and biodiesel characterization.

2. Material and methods

2.1. Chemicals and raw material

LGCPO was obtained from a local mill, Selangor Darul Ehasn, Malaysia. Potassium hydroxide (KOH) pellets 85%, magnesium sulfate ($MgSO_4$) and methanol 99.8% were purchased from R&M Chemicals. Laboratory grade allyltriphenylphosphonium bromide ($C_{21}H_{20}BrP$) 99% and *p*-toluenesulfonic acid monohydrate (PTSA) ($C_7H_8O_3S \cdot H_2O$) ≥ 98% were purchased from Merck and Sigma-Aldrich.

2.2. DES preparation

Allyltriphenylphosphonium bromide and PTSA were dried at 60 °C under vacuum, and then mixed together in a molar ratio of 1:3 salt to PTSA. A glass jacketed vessel with mechanical stirrer was used to prepare P-DES at a temperature of 80 °C and a stirrer rate of 300 rpm for 3 h. The final mixture of P-DES was in a jelly–viscous form at room temperature and yellow color, Fig. 1. The preparation was carried out in a fume hood.

2.3. Synthesis of biodiesel from LGCPO

Two catalyzed reactions, i.e. esterification and transesterification, were performed to produce biodiesel from LGCPO. In the esterification reaction, P-DES was utilized as a catalyst, Fig. 2, to reduce FFA content to less than 2% while in the transesterification reaction KOH was used as a catalyst. P-DES was added to the methanol and then mixed with the pre-heated LGCPO. P-DES was added at different dosages between 0.25 and 3.5 wt/wt%. Other operating conditions such as molar ratio, reaction temperature and reaction time were optimized in the range of 1:1–20:1, 40–80 °C, 0–120 min, respectively.

At room temperature LGCPO existed as a viscous phase; therefore it was heated to 70 °C. The pre-heated LGCPO was then transferred into the batch multi-unit reactor system for the esterification reaction. After each experiment, the FFA content was measured in order to evaluate the operating conditions. A catalyst recyclability study was conducted in order to determine the catalytic activity of P-DES after the esterification reaction using the optimum operating conditions. The treated LGCPO was then used in the transesterification reaction to produce biodiesel fuel. The reaction conditions for transesterification were fixed according to Hayyan et al. (2010b). After reaction, the product (FAME, methanol and crude glycerol) was directly transferred to the rotary evaporator to remove the excess methanol. After evaporation the FAME and glycerol were settled overnight to separate the FAME than crude glycerol.

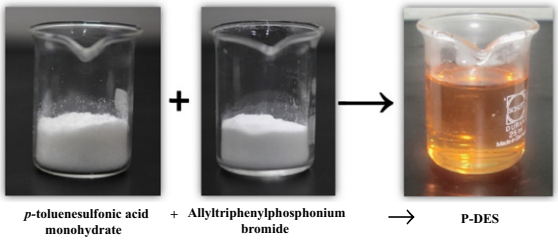

Fig. 1. Synthesis of P-DES. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

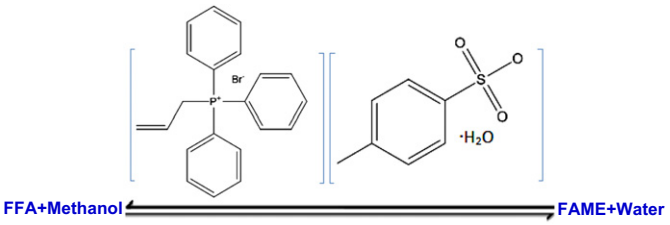

Fig. 2. Esterification reaction using P-DES.

Table 1
Fatty acids composition of LGCPO.

Fatty acids	Structure	Type of fatty acid	Fatty acids (wt%)
Lauric acid	C12:0	Saturated	0.30
Myristic acid	C14:0	Saturated	1.10
Palmitic acid	C16:0	Saturated	44.5
Palmitoleic	C16:1	Unsaturated	0.48
Stearic acid	C18:0	Saturated	3.98
Oleic acid	C18:1	Unsaturated	39.95
Linoleic acid	C18:2	Unsaturated	9.13
Alpha-linolenic acid	C18:3	Unsaturated	0.23
Arachidic acid	C20:0	Saturated	0.316

Due to differences in the viscosity and density of the two products, two layers were formed in the separating funnel. The upper layer was the biodiesel (FAME) while the lower layer consisted of crude glycerol. The separation time was fixed to 24 h in order to purify the FAME layer from the free glycerol and other impurities which can negatively affect the final quality of biodiesel. The FAME was purified *via* a washing technique. The traces of water present in the product were absorbed using $MgSO_4$. The final product was then analyzed according to the official standard analysis methods (ASTM D6751 and EN 14214). Each experiment after the esterification reaction was carried out in a lab scale multi-unit reactor system. The temperature of the jacketed vessel and motor speed were controlled using a dedicated feedback control system.

3. Chemical analysis

The American Oil Chemist's Society (AOCS) official method Ca 5a-40 for commercial fats and oils was used to calculate the FFA content (American Oil Chemists' Society (AOCS), 1997). The melting point of P-DES was measured using a melting point apparatus (SASTEC^{TM}, Model: ST-WRS-2A, Malaysia). The fatty acids profile in LGCPO was measured using a GC/MS (Agilent Technologies 7890A gas chromatograph equipped with 5975C mass spectrometer). One microliter of neat sample was diluted in hexane prior to injection into GC. The ester content was analyzed using a GC/FID (Perkin Elmer Clarus 500), split—splitless mode of injector, capillary column, isotherm oven at 250 °C. Mono-, di-, and tri-acylglycerols (MG, DG and TAG), free and total glycerol content were measured using GC/FID (Perkin Elmer Clarus 500). An oven temperature program up to 350 °C setting was used to detect trace compounds. Catalyst loading was determined as the weight ratio of used catalyst to that of the product in milligram.

4. Results and discussion

4.1. Fatty acid profile of LGCPO

The LGCPO carbon chains were estimated and reported in Table 1. According to Table 1 the main fatty acids are oleic, palmitic, linoleic and stearic acid. These types of fatty acids are the main constituents of palm oil (Sambanthamurthi et al., 2000). Saturated and unsaturated fatty acids in LGCPO are present in equal quantities. It was reported that CPO with FFA content of 3.49% has 53.54% saturated fatty while the corresponding reported values of SPO were 22.33% FFA content with 47.17 wt% (Elsheikh et al., 2011; Hayyan et al., 2010a). Due to the high FFA and saturated fatty acids content, the LGCPO exists as a viscous red liquid. Therefore, heating of LGCPO before processing was a very useful technique to reduce its high viscosity. Heating the acidic oils such as ACPO before esterification reaction was also recommended by Hayyan et al. (2010a, 2011a, 2012a).

4.2. Esterification of LGCPO using P-DES

Esterification reaction was carried out in order to achieve the acceptable industrial limit of FFA content. The acid catalyst dosages, molar ratio, reaction temperature, reaction time and mixing intensity are the main parameters affecting the esterification reaction. Fig. 2 shows the esterification reaction for the pre-treatment of LGCPO using P-DES catalyst. In order to confirm the successful synthesis of P-DES, the melting point (M.P.) was measured and it was in the range of 43–47 °C which is much lower than the corresponding values of the individual constituting compound (phosphonium salt and PTSA). This reduction in M.P. after mixing confirmed the formation of P-DES. The formation of the P-DES (Fig. 1) was due to the hydrogen bonding between phosphonium salt and the hydrogen bond donor (PTSA). These bonds tend to dislocalize the charge distribution around the salt molecule causing a reduction in melting point.

4.2.1. Effect of P-DES catalyst

The P-DES catalyst dosage was optimized in the range of 1–3.5 wt%. The FFA content limit was fixed to the recommended FFA content, i.e. 2% (Hayyan et al., 2010a, 2011a). Fig. 3 shows the effect of P-DES in LGCPO towards the yield of treated oil, FFA content and their conversion to FAME. As mentioned above, the FFA content in LGCPO was 9.3%. This amount was reduced after a low loading of catalyst to LGCPO (such as 0.25% and 0.5%), however, the FFA content was still high and above the target limit. Using a catalyst dosage of 0.25%, 0.5% and 0.75%, the achieved residual FFA content was 4.12%, 3.072% and 2.677%, respectively. On the other hand, when the catalyst dosage was increased to 1% of P-DES to LGCPO, the FFA content was reduced significantly to less than 2%. This high catalytic strength is sufficient to treat the LGCPO during the course of the esterification reaction. It was also found that small concentrations of TAG (less than 10%) in LGCPO, can be converted to FAME using 1% of P-DES. There was no enhancement in the treated LGCPO yield after pre-treatment and it was within the range of 93–97%. Based

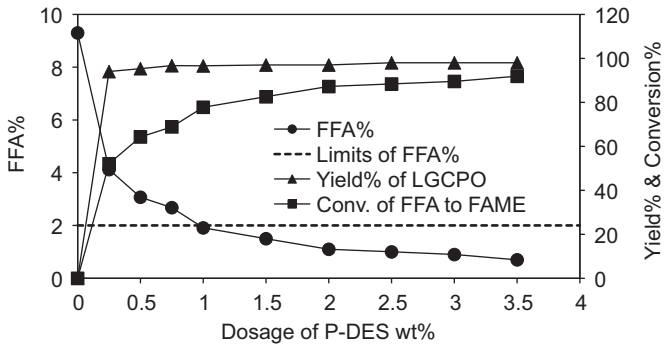

Fig. 3. Effect of P-DES dosage on the FFA reduction and yield of treated LGCPO at 10:1 M ratio, 60 °C reaction temperature, 30 min reaction time and 300 rpm stirrer speed.

on the yield of treated LGCPO, 1 wt/wt% (P-DES to LGCPO) resulted in 1.91% FFA content and the treated LGCPO yield was 96.6% and a FAME conversion was 79.4%. It is worth mentioning that Hayyan et al. (2010a) used 0.75% of PTSA to reduce the high FFA content (22.33%) in SPO to less than 2% while Di Serio et al. (2008) used 6.4×10^{-5} mol of PTSA to treat the FFA content in soybean oil from 20.5% to 1.1%.

4.2.2. P-DES catalyst loading

Reducing the industrial production cost is the main target to any viable industrial application. Hence, in order to demonstrate the economic feasibility of the pre-treatment process using P-DES, the catalyst loading was calculated. Catalyst loading (C.L.) is an economic factor which plays an essential role in the overall biodiesel production cost. The results for C.L. with the dosage of P-DES catalyst, FAME conversion and yield of treated LGCPO are presented in Fig. 4. High yield and FAME conversion (of 2.77 and 5.35 mg/g respectively) were obtained with a proportional increase of catalyst dosage and C.L. at 0.25% and 0.5% respectively. However, using a P-DES dosage of 0.5% resulted in a low FAME conversion and yield as shown in Fig. 4. The LGCPO yield and the FAME conversion increased slightly using a P-DES dosage of 0.75%. Fig. 4 portrays that the treated LGCPO yield and the FAME conversion increased with increase in the catalyst dosage to 1%. An amount of 10.34 mg of P-DES is required to produce 1 g of treated LGCPO at 1% P-DES to LGCPO, which indicated that this dosage is the optimum acid dosage for the esterification reaction. There was no significant enhancement in the treated LGCPO yield or the FAME conversion when the dosage of catalyst was increased to more than 1%. Lower loading of catalyst will contribute in reducing the cost of biodiesel production. In addition, C.L. results support the selection of an optimum dosage of 1% P-DES to LGCPO. C.L. of catalyst can be used for other studies related to catalyst activity analysis.

4.2.3. Molar ratio effect

Sufficient molar ratio should be provided in order to effectively complete the esterification reaction. The esterification reaction stoichiometry (Fig. 2) shows an ideal molar ratio of 1:1. Practically, this ratio is not enough to reduce the high FFA content in acidic oils such as LGCPO. Therefore, the methanol loading was varied at different ratios (from 1:1 to 20:1) as shown in Fig. 5. Low loading of methanol such as 1:1 or 1:5 resulted in a low reduction in FFA content. Based on these results, reacting the FFA with insufficient amount of methanol, the reaction tends to be slower, thus decreasing the FAME conversion significantly. A molar ratio of 10:1 can reduce the FFA content significantly to less than 2%. Molar ratio more than 10:1 did not enhance the FFA reduction. Therefore, in order to minimize the consumption of methanol and

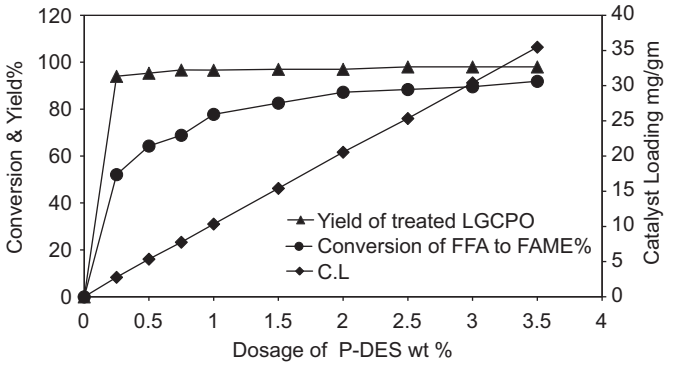

Fig. 4. Effect of P-DES dosage on the yield of treated LGCPO, conversion of FFA to FAME and catalyst loading.

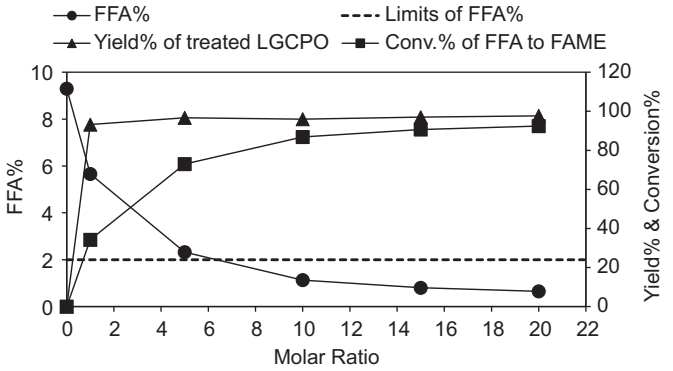

Fig. 5. Effect of molar ratio on the FFA reduction, conversion of FFA to FAME and the yield of treated LGCPO at 1% dosage of P-DES to LGCPO, 60 °C reaction temperature, 30 min reaction time and 300 rpm stirrer speed.

to save the energy required to evaporate the excess methanol, 10:1 M ratio is selected as the optimum ratio for the pre-treatment LGCPO using P-DES. At this molar ratio the FFA content was reduced from 9.3% to 1.10% and the FAME conversion was 88.1%, while the yield of treated LGCPO was in the range of 94–98% and there is no significant reduction achieved at higher molar ratios. Hayyan et al. (2010a) used PTSA to treat the high FFA content in SPO and their study reported a similar optimum molar ratio. Man et al. (2013) used 15:1 to treat the FFA content (3.49%) in CPO.

4.2.4. Reaction temperature effect

Reaction temperature has an important role in the enhancement of chemical reactions such as esterification. The esterification temperature was varied from a low temperature of 40 °C to a high temperature of 80 °C, Fig. 6. This is to understand the temperature effect on the progress of the reaction. In addition, the results may be used for a further reaction kinetics investigation. As shown in Fig. 6, a reaction temperature of 80 °C shows a negative effect and the FFA content was 2.07. On the other hand, a reaction temperature of 70 °C resulted in an FFA content of 1.44% which is with the industrial acceptable limit. A lower reaction temperature of 40°C shows low conversion and FFA content reduction. An FFA conversion to FAME of 3.75% and 2.57% were obtained for the temperatures 40 °C and 50 °C respectively. To optimize the energy requirements of the reaction, a reaction temperature of 60 °C was selected. At this temperature, a high yield of treated LGCPO and conversion of FFA to FAME was obtained, with a 1.52% FFA reduction. Other studies reported a similar reaction temperature as the optimum for the esterification of acidic oils (Hayyan et al., 2010a, 2011a, 2011b, 2012a).

4.2.5. Effect of reaction time

The reaction time is a very important operating parameter due to its direct effect on the cost and quality of biodiesel. Sufficient but not excessive reaction time must be provided to achieve a complete and perfect reaction. The esterification reaction time was optimized in the range of 3–120 min (Fig. 7). Other conditions were fixed to be 1% dosage of P-DES to LGCPO, 10:1 M ratio, 60 °C reaction temperature and 300 rpm stirrer speed.

There is no significant effect on the yield of treated LGCPO after 30 min of reaction time. It was found that the majority of FFA content in LGCPO was removed within the first 30 min. 30 min reaction time can serve as the optimum reaction time for the esterification of LGCPO. Half an hour of reaction time is sufficient to decrease the FFA content from 9.3% to less than 1%. The yield of treated LGCPO was 96% with a 88.95% FAME

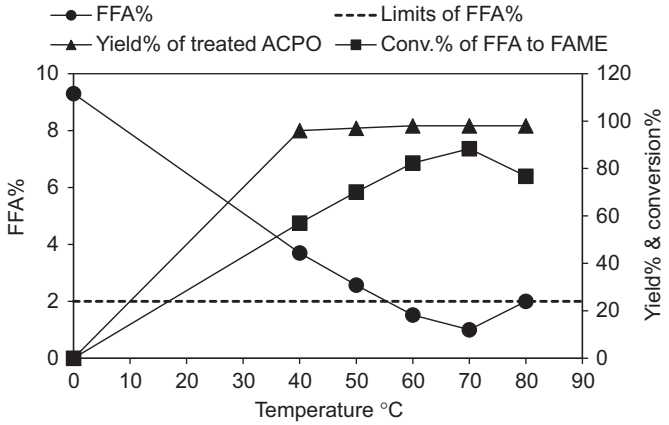

Fig. 6. Effect of reaction temperature on the FFA reduction, conversion of FFA to FAME and the yield of treated LGCPO at 1% dosage of P-DES to LGCPO, 10:1 M ratio, 30 min reaction time and 300 rpm stirrer speed.

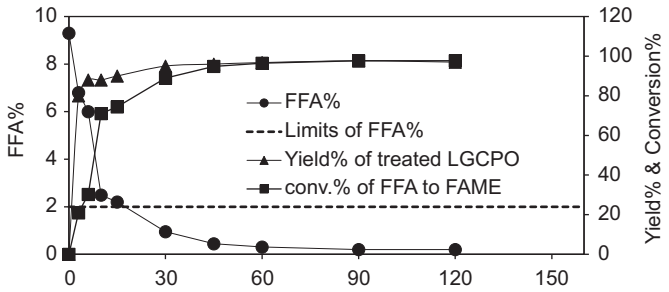

Fig. 7. Effect of reaction time on the FFA reduction, conversion of FFA to FAME and yield of treated LGCPO at 1% dosage of P-DES to LGCPO, 10:1 M ratio, 60 °C reaction temperature and 300 rpm stirrer speed.

conversion. This indicates that the consumption rate of FFA in LGCPO was found to be short. The results shown in Fig. 7 indicated that additional reaction time more than 30 min did not contributed in improving the reaction. The fact that short reaction time is needed to complete the reaction indicates the high catalytic activity of P-DES due to the presence of the sulfonic group SO_3H from hydrogen bond donor (PTSA). The current results are much better than those reported by a recent application of the IL 1-butyl-3-methyl-imidazolium hydrogensulfate [bmim][HSO_4] and triethylammoium hydrogensulfate (Et_3NHSO_4) in the pre-treatment of FFA in CPO (Elsheikh et al., 2011; Man et al., 2013). The reaction time required to reduce the FFA content to the minimum limit was 120 min using [bmim][HSO_4] and 180 min using (Et_3NHSO_4) (Elsheikh et al., 2011; Man et al., 2013). The short reaction time for the esterification of LGCPO will decrease the cost of the pre-treatment process significantly.

4.2.6. Validation of optimum conditions and catalyst recyclability study

The optimum esterification operating conditions using P-DES were 1% (wt/wt) P-DES to LGCPO, 10:1 M ratio, 60 °C temperature, and 30 min reaction time. At these reaction conditions, 0.88% FFA content was achieved, with 96% yield of treated LGCPO and 90.53% FAME conversion. The yield of the final product after transesterification and purification was 89.84% with 0.06% FFA and 97% ester content. Fig. 8 shows the FAME high conversion using P-DES in the esterification of LGCPO within the first three recycle runs. It can be seen from Fig. 8 that the forth recycle run was slightly lower in terms of FAME conversions due to loss of catalyst as a consequence of reuse. The catalyst loading decreased due to some losses when the reactant was transferred between units as well as the traces of catalyst remaining in the treated LGCPO. This change in catalyst loading has considerable influence on the equilibrium FAME conversion which explains the variation in reaction time among the different reaction cycles. Therefore, in order to achieve the target (2% FFA content) without using new dosage of catalyst, high loading of methanol as well as an increase in the reaction time are recommended. The main advantage of using P-DES is due to its recyclability. Using PTSA alone as a catalyst will not facilitate its recycling due to its loss in the product.

4.3. Transesterification reaction of treated LGCPO

The alkaline transesterification reaction was carried out in order to convert the TAG of treated LGCPO to FAME. During reaction the traces of FFA were also converted to FAME. Table 2 gives the fatty acid composition of biodiesel from treated LGCPO. The FAME carbon chains starts from C12:0 (Lauric acid) and ends with C20:0 (Arachidic acid). It was noted that the saturated fatty acid was high in the final product which makes the LGCPO a suitable raw material for biodiesel production. As saturated fatty acids increase, the cetane number will increase and oxidation will decrease (Canakci and Gerpen, 2001). Table 3 shows the specification of biodiesel. It was noted that elements such as potassium (K) and phosphorus (P) were of low concentration and within the acceptable limit for biodiesel fuel. Sulphated ash was also analyzed and the result showed that the fuel contains less than 0.005% which is below the acceptable limit of 0.02%. These results confirmed that the P-DES was completely removed from the biodiesel. The corrosion issue is very important for adopting any new technology. The copper strip

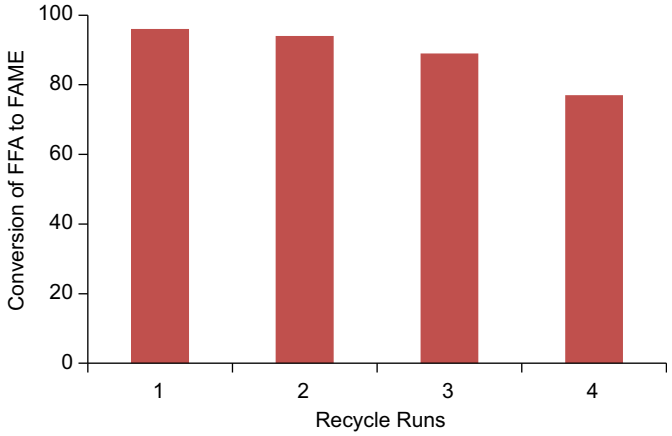

Fig. 8. FFA to FAME conversion at different catalyst recycling runs at 1% dosage of P-DES to LGCPO, 10:1 M ratio, 60 °C reaction temperature, 30 min reaction time and 300 rpm stirrer speed.

Table 2
Fatty acids profile of biodiesel from LGCPO.

Fatty acid methyl ester	Structure	Fatty acids (wt%)
Lauric acid methyl ester	C12:0	0.22
Myristic acid methyl ester	C14:0	1.03
Palmitic acid methyl ester	C16:0	41.77
Palmitoleic methyl ester	C16:1	0.046
Stearic acid methyl ester	C18:0	5.097
Oleic acid methyl ester	C18:1	41.44
Linoleic acid methyl ester	C18:2	9.68
Alpha-linolenic acid methyl ester	C18:3	0.24
Arachidic acid methyl ester	C20:0	0.43

Table 3
Specifications of biodiesel from LGCPO.

Properties	Biodiesel from LGCPO	EN 14214		ASTM D6751	
		Test method	Limits	Test method	Limits
Ester content	97% (mol mol^{-1})	EN 14103	96.5% (mol mol^{-1}) min	–	–
Monoacylglycerol content	0.06% (mol mol^{-1})	EN 14105	0.80% (mol mol^{-1}) max	–	–
Diacylglycerols content	0.02% (mol mol^{-1})	EN 14105	0.20% (mol mol^{-1}) max	–	–
Triacylglycerols content	< 0.01% (mol mol^{-1})	EN 14105	0.20% (mol mol^{-1}) max	–	–
Free glycerol content	< 0.01% (mol mol^{-1})	EN 14105	0.02% (mol mol^{-1}) max	ASTM D 6584	0.020% (w/w) max
Total glycerol content	0.05% (mol mol^{-1})	EN 14105	0.25% (mol mol^{-1}) max	ASTM D 6584	0.240% (w/w) max
Water content	411 mg kg^{-1}	EN ISO 12937	500 mg kg^{-1} max	ASTM D 2709	0.050% (v/v) max
K content	1 mg kg^{-1}max	EN 14108	5.0 mg kg^{-1}max	UOP 391	5.0 mg kg^{-1}max
P content	7.2 mg kg^{-1} max	EN 14107	10.0 mg kg^{-1} max	ASTM D 4951	0.001% (w/w) max
Density (15 °C)	874.5 kg m^{-3}	EN ISO 3675	860–900 kg m^{-3}	–	–
Flash point	182.9 °C	EN ISO 3679	120 °C min	ASTM D 93	130 C min
Cloud point	15.67 °C	–	–	ASTM D 2500	Not specified
Sulphated ash	< 0.005% (w/w)	ISO 3987	0.02%v(mol mol^{-1}) max	ASTM D 874	0.020% (w/w) max
Total contamination	0.0085 mg kg^{-1}	EN 12662	24 mg kg^{-1} max	–	–
Acid value	0.12 mg KOH g^{-1}	EN 14104	0.50 mg KOH g^{-1} max	ASTM D 664	0.50 mg KOH g^{-1}max
Iodine value	50.33 g I2 · 100 g^{-1}	EN 14111	120 g I2 · 100 g^{-1} max	–	–
Copper strip corrosion (3 h at 50 °C)	Class 1	EN ISO 2160	Class 1 rating	ASTM D130	No. 3 max

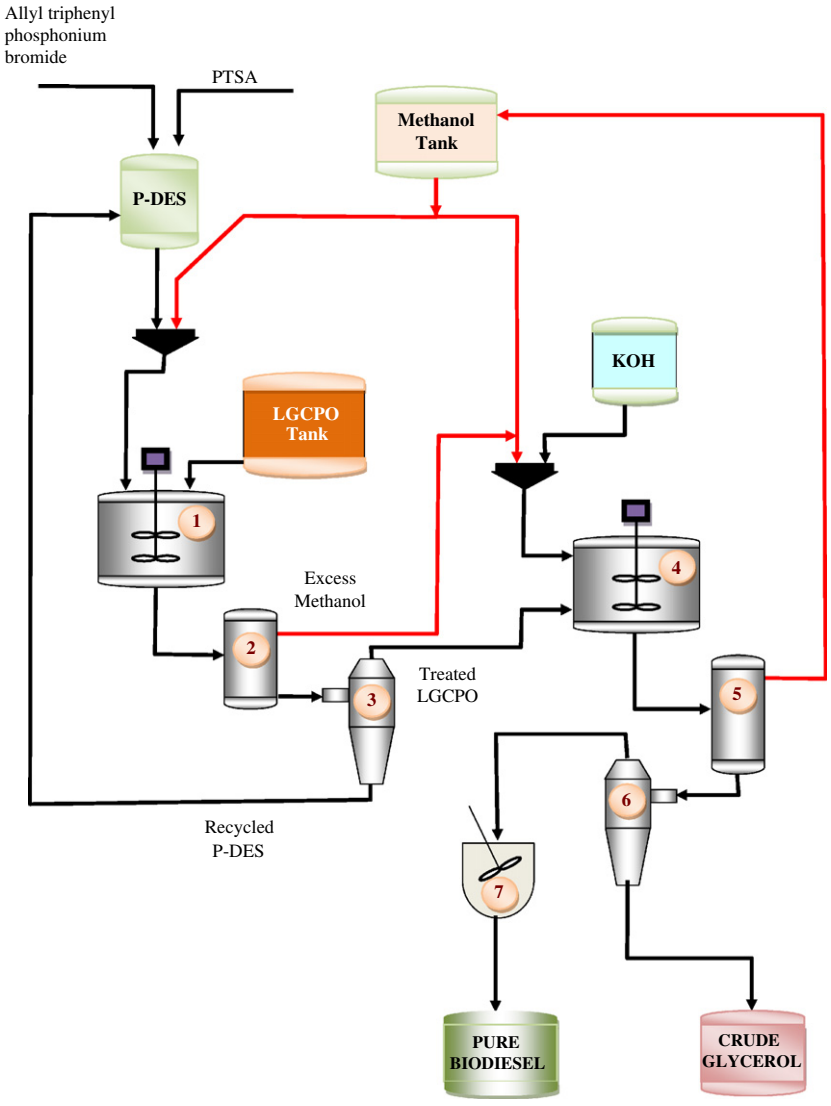

Fig. 9. Proposed schematic for the pre-treatment and biodiesel production form of LGCPO using P-DES. 1. Esterification reactor, 2. evaporator, 3. centrifuge, 4. transesterification reactor, 5. evaporator, 6. centrifuge, and 7. washing vessel.

corrosion was class 1 which is acceptable for the international standard of biodiesel fuel. The ester content was 97% mol mol^{-1} which indicates that the two reactions were able to successfully convert the FFA and TAG to FAME.

4.4. Suggested process plant layout

Fig. 9 shows the layout of the proposed LGCPO pre-treatment process. In order to prepare the P-DES, a teflon coated mixer is recommended in mixing the PTSA and P-salt.

The process consists mainly of an esterification and transesterification reactors, an evaporator to remove the excess methanol and the free water produced as by-product from first and second reactions, a centrifuge to recover the catalyst and separate the two phases (biodiesel and crude glycerol) and finally, a washing vessel to purify the crude biodiesel produced after transesterification reaction.

It is recommended more to melt the LGCPO before sending it to esterification reaction. The esterification reactor output is transferred to the evaporator followed by the centrifuge to recover the catalyst. The treated LGCPO is then fed to the transesterification reactor and potassium methoxide is added to carry out the reaction. Untreated biodiesel and the crude glycerol are fed to the evaporator and centrifuge in order to purify the products from excess methanol and to facilitate fast separation. The crude biodiesel is finally fed to the washing vessel to purify the product from contaminants, soap and traces of crude glycerol. The studied P-DES will be then recycled for four times with the same experimental conditions as indicated previously. The temperature is set at 60°C, and the molar ratio to 10:1.

Water heated at 60–70 °C was used in this study for the purification process. Other washing techniques can be studied and applied in this particular stage of downstream. We used a novel technique for the purification of palm oil based biodiesel using DES (Hayyan et al., 2010b). Consequently, we can say that DES can be used in the upstream as a catalyst and as a washing solvent in the downstream process. This multi-purpose DES system can be proposed for improving the biodiesel production industry.

5. Conclusion

This study demonstrated the viability of using LGCPO produced from industrial palm oil mills for biodiesel production using a two-stage reaction. P-DES was introduced as a catalyst to treat the high FFA content in LGCPO for biodiesel production. Lab-scale experiments were carried out to treat LGCPO. The treated LGCPO was then utilized as the raw material for the transesterification reaction. It was found that P-DES can serve as a promising catalyst in the development of biodiesel pre-treatment processes. The optimum conditions for the esterification reaction were 1 wt% P-DES, 10:1 methanol to LGCPO, reaction temperature of 60 °C and 30 min reaction time. These optimum conditions reduced the FFA from 9.3% to less than 2%. The esterification product achieved 0.88% FFA content, with 96% yield of treated LGCPO and 90.53% FAME conversion. The properties of the final product after transesterification and purification of biodiesel was 89.84% with 0.06% FFA and 97% ester content. The biodiesel produced from LGCPO meets the international standards (ASTM D6751 and EN 14214). Further studies are needed for testing the P-DES catalyst for biodiesel production in a pilot plant scale.

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